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Spinodal Decomposition in Al/Zn Alloys

Part 2 *X-ray Diffraction Studies*

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Spinodal decomposition was studied by X-ray diffraction in Al/Zn alloys over the range of 30 to 60 wt % zinc. The spinodal structures were extremely anisotropic with respect to X-rays and were found to form during the quench. The periodicity of the structure was determined for a number of ageing treatments.

The spinodal structure was very stable at room temperature in the dilute alloys but decomposed rapidly in both Al/50% Zn and in Al/60% Zn. The stability varied inversely with zinc content. Breakdown of the modulated structure occurred by zinc precipitation.

1. Introduction

A knowledge of the nature of the spinodal structure in Al/Zn alloys was necessary in order to explain the mechanical behaviour described in the preceding paper [1]. It was also of interest to follow the breakdown of the modulated structure during ageing and to assess the relative stabilities amongst the various alloys. This paper presents a summary of X-ray diffraction studies performed in support of the mechanical property study.

2. Experimental Procedures

Preparation of the alloys and techniques used in the ageing studies have been described previously [1]. X-ray diffraction studies were made on a Norelco diffractometer with filtered copper radiation. The samples were mounted in a sample spinner that was manually rotated until the maximum intensity of the desired peak was obtained. The traverse was then made with the sample stationary. Ageing experiments were performed in the diffractometer, which was oscillated over a predetermined range of 2θ by using the stops and reversing switches on the instrument.

3. Results

3.1. Precipitation of Zinc

In all cases the metastable solid solution was preserved upon quenching from the solution-treatment temperature. X-ray diffraction revealed no zinc lines for the shortest times studied at 22° C, about 4 min. Typical traverses for the 38.5, 50, and 60% Zn alloys are shown in figs. 1, 2a, and 3a, respectively. Samples aged at 100° C were initially quenched to 22° C and immediately reheated to 100° C. A trace of zinc was detected after ageing for 1 min in both the 50 and 60% Zn samples. However, the 38.5% Zn alloy was considerably more stable than the higher zinc alloys, and no evidence of zinc was found until about 1000 min had elapsed at 100° C. The most intense zinc reflection (101) can be seen in 50% Zn after ageing 4 min (fig. 3b). This reflection was more intense in 60% Zn after ageing for 1 min, and this sample also showed a trace of the (002) peak (fig. 3b).

Increasing the ageing time caused an intensification of the (101) peak as well as the appearance of other zinc peaks. These transitions can be seen in figs. 2 and 3. The times at which the first zinc peaks were detected for these alloys aged at room temperature were 1000 and 10 min for 50 and 60% Zn samples, respectively. The stability of the quenched solid solution obviously decreased notably with increasing zinc content. The 38.5% Zn alloy was considerably more stable than the 50% Zn alloy, as fig. 1 shows; no zinc was present after 400 000 min at room temperature. The 30% Zn alloy appeared to be as stable as the 38.5% Zn alloy, although the maximum

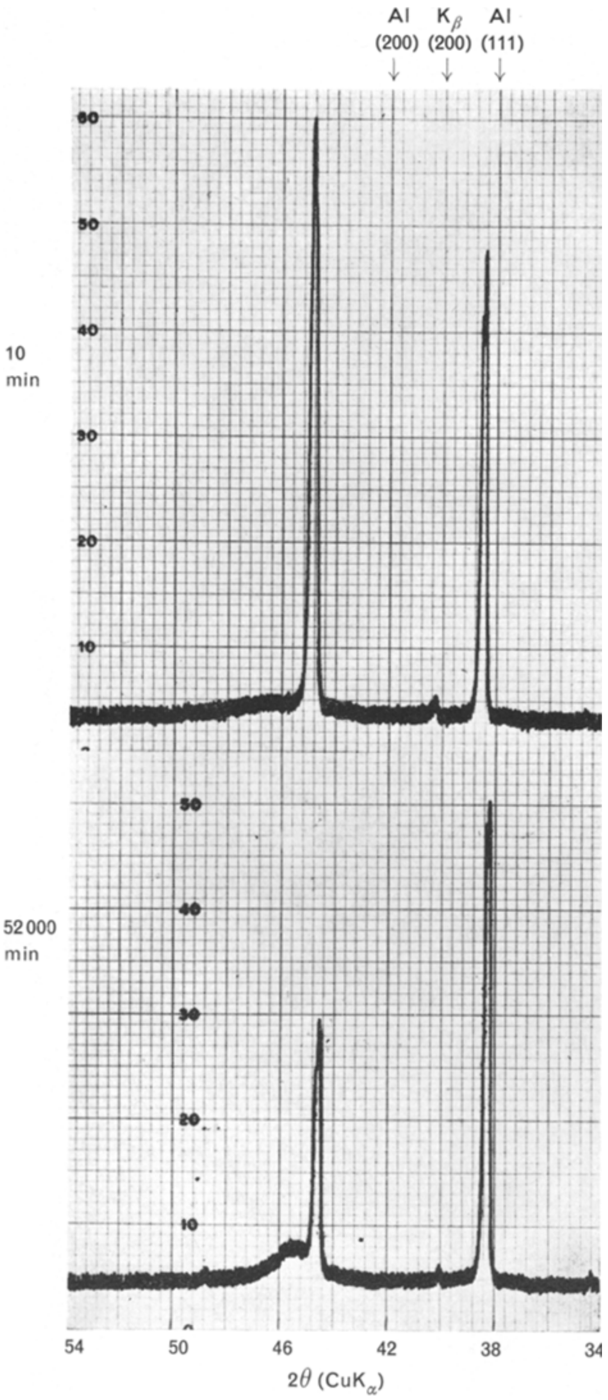


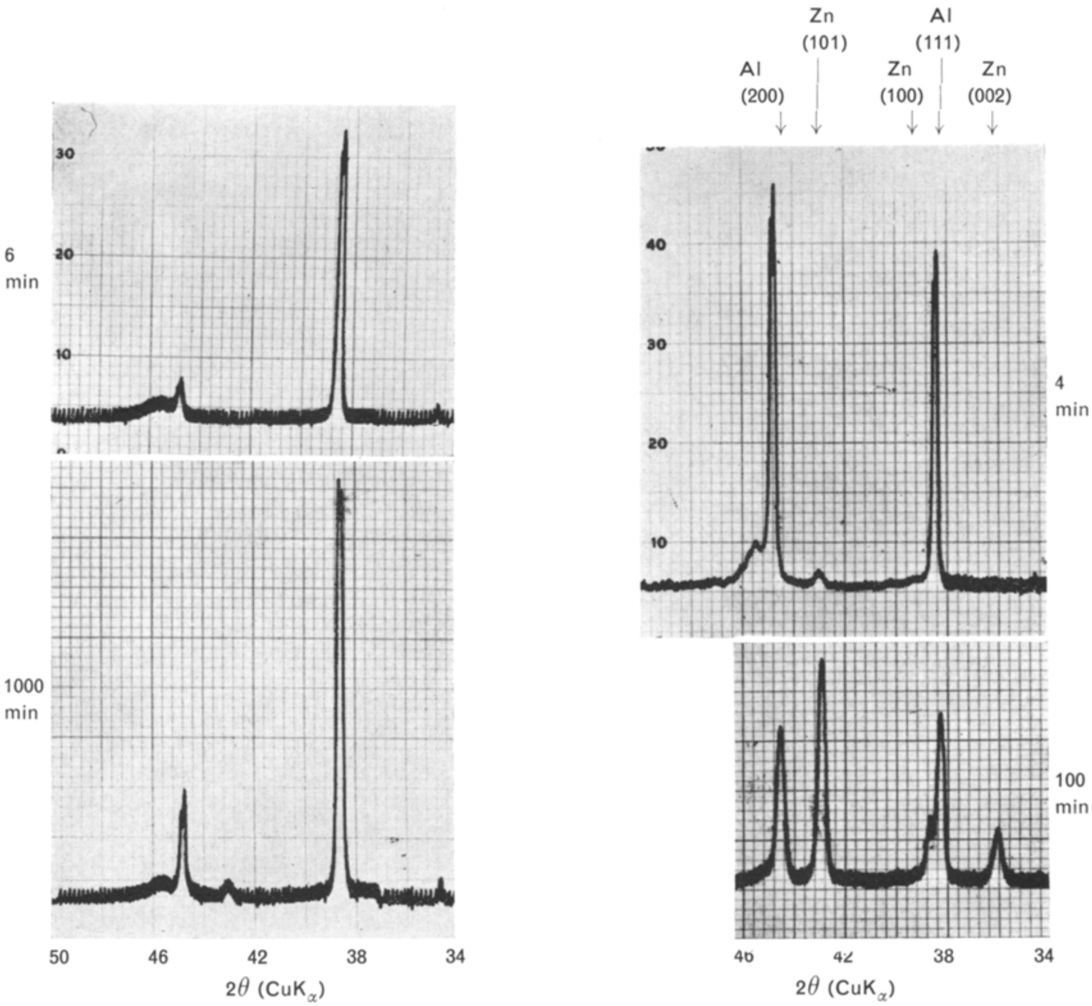
Figure 1 X-ray diffraction patterns of Al/38.5% Zn quenched from 365° C and aged at 22° C.

time at which the former was studied was only 220 000 min. There was no evidence of zinc precipitation during this period.

The decomposition of the metastable 60% Zn solid solution at room temperature was followed on a given sample by oscillating the diffractometer back and forth over a range of about 3° 2θ. The sample orientation and all settings on the diffractometer were kept constant throughout the test. The sequence (fig. 4) shows the $(1\,1\,1)_{\mathrm{Al}}$ peak resolved into the $\mathrm{K}_{\alpha 1} - \mathrm{K}_{\alpha 2}$ doublet. The intensity of the (1 1 1) peak decreased with time (fig. 5), and another fcc phase, which was richer in Al than the quenched solid solution, began to precipitate. Zinc precipitation was also occurring. The zinc peak was obscured by the (1 1 1) peak of the metastable solid solution, but its presence was ascertained by the observation of another zinc peak (1 0 1) that was not obscured. The aluminium-rich phase was strained, as the broadened peak shows. This peak was on the low-angle side of the original (1 1 1) peak as is to be expected from the fact that zinc decreased the lattice parameter of aluminium. Eventually the original (1 1 1) peak disappeared, and the (1 0 0) zinc peak appeared. This peak was also broadened. The broadening most likely arises from the coherency strains between zinc and aluminium. Slight shifts in the interplanar spacings were noted, but the broadness of the back reflection peaks did not permit more than a qualitative assessment of the change. Both the zinc and aluminium lattices expanded as a function of time. Zinc decreases the lattice parameter of aluminium; hence one would expect this parameter to increase as zinc is precipitated. This increase has been observed by Rao and Herman [2] during the ageing of Al/25% Zn at 100° C. According to the phase diagram there is negligible solubility of aluminium in zinc at 100° C, and it is expected that nearly pure zinc will precipitate. The slightly expanded zinc lattice may also be due to coherency of the zinc with the aluminium matrix.

3.2. Structural Anisotropy

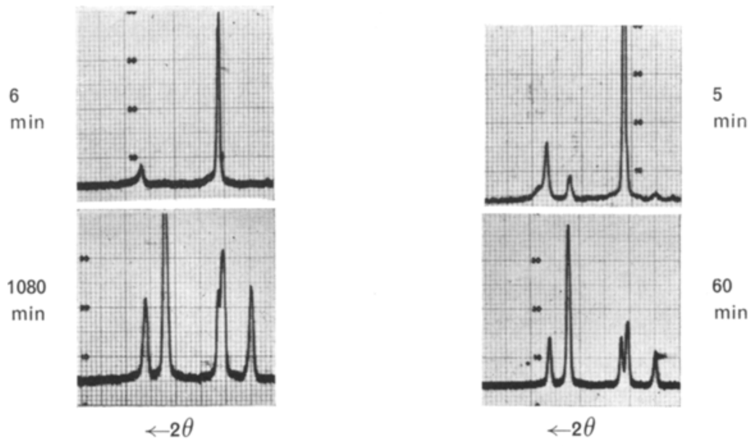
The intensity of the $(1\,1\,1)_{\mathrm{Al}}$ and $(2\,0\,0)_{\mathrm{Al}}$ peaks of the metastable solid solution is strongly dependent upon the orientation of the specimen relative to the plane of the diffractometer. A spinning device was used so that the sample could be manually rotated to give maximum intensity. The diffraction patterns were always made at the particular setting for maximum intensity. The variation of intensity of the $(1\,1\,1)_{\mathrm{Al}}$ peak in 50% Zn quenched from 435° C and aged



(a)

(b)

Figure 2 X-ray diffraction patterns of Al/50% Zn quenched from 435° C and aged at (a) 22° C and (b) 100° C.



(a)

(b)

Figure 3 X-ray diffraction patterns of Al/60% Zn quenched from 435° C and aged at (a) 22° C and (b) 100° C.

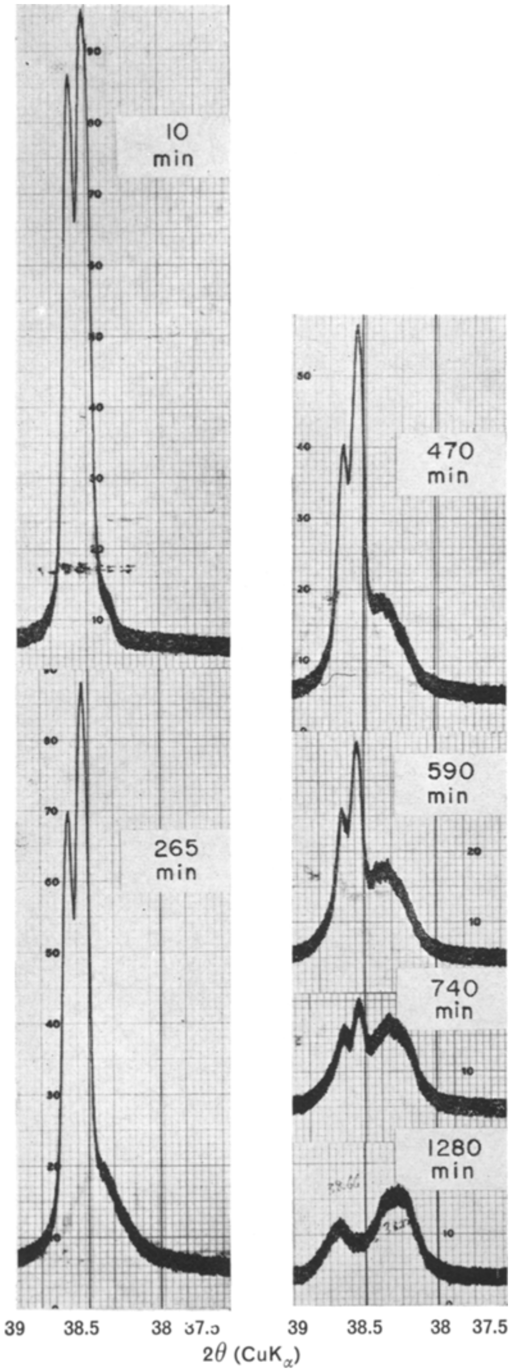


Figure 4 Decomposition of Al/60% Zn metastable solid solution quenched from 435° C and aged at 22° C.

2 min at 100° C is shown as a function of orientation in fig. 6. The peak completely disappeared when the sample was rotated a few degrees.

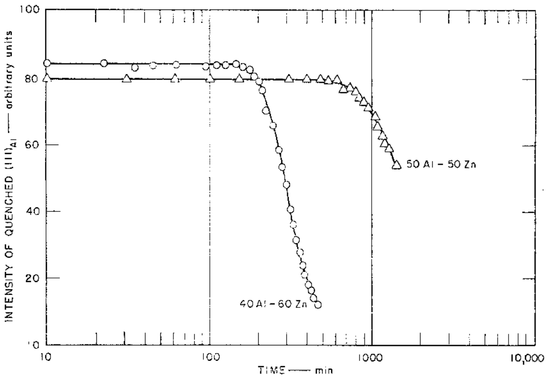


Figure 5 Change of X-ray intensity of $(111)_{Al}$ quenched solid solutions during ageing at 22° C (samples quenched from 435° C).

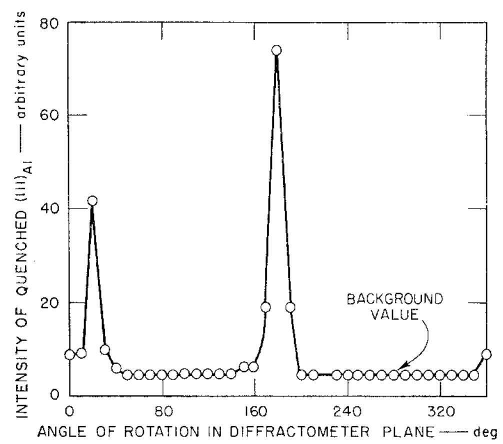
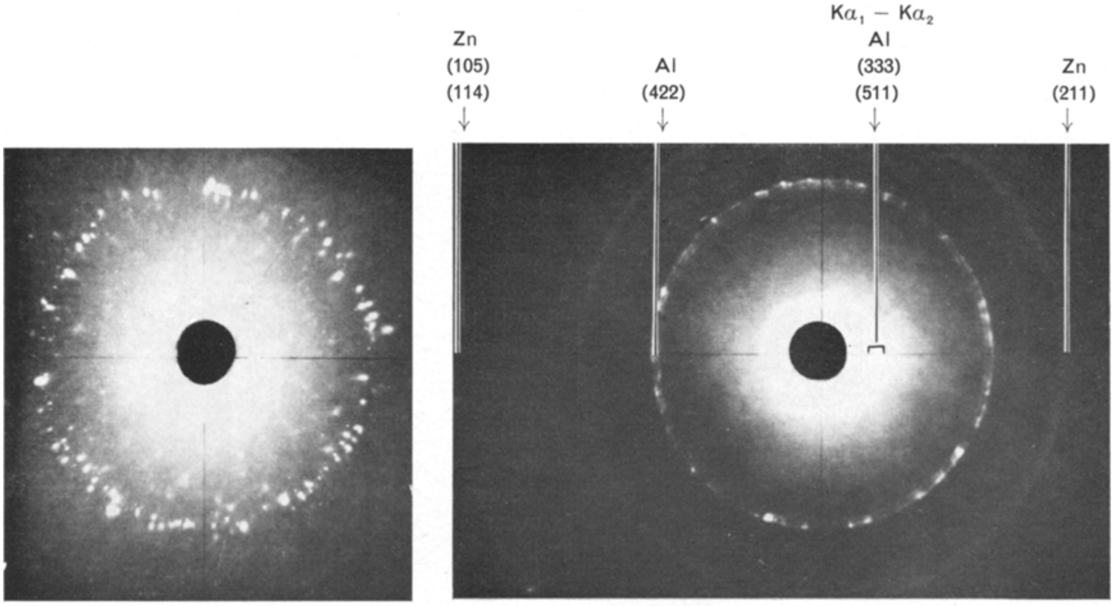


Figure 6 Orientation sensitivity of X-ray samples for quenched solid solutions (Al/50% Zn quenched from 435° C and aged 2 min at 100° C).

A further investigation of the anisotropy was made by Laue back-reflection photograms. A typical pattern, fig. 7, showed that the matrix was polycrystalline and randomly oriented, but there were high intensity spots on some of the aluminium rings. This indicates that a highly oriented, aluminium-rich precipitate also existed in the structure.

3.3. Spinodal Structure

The presence of a spinodal structure is verified by the presence of X-ray sidebands [3] on reflections of the type (h00). The sidebands arise from the periodic, modulated compositional variations of the spinodal structure. Sidebands were clearly visible on the high-angle side of the



(a) (b)

Figure 7 Laue back-reflection patterns of Al/30% Zn solution-treated 1 h at 365° C. (a) Spinodal structure: 20 weeks at 22° C. (b) Overaged structure: 2000 min at 100° C.

Al $_{(200)}$ peak but were partly occluded on the low-angle side. Typical sidebands are shown in fig. 8.

The spinodal structure was very stable at 22° C in both the 30 and 38.5% Zn alloys, for times of at least 220 000 and 400 000 min, respectively. The stability in 50% Zn was considerably less, as is evidenced by a decrease in the intensity with ageing time, the sidebands disappearing within 1 or 2 days. The stability at higher temperatures was of course much less than at 22° C and also decreased with increasing zinc content.

The periodicity of the spinodal structure can be measured from the relationship [3]:

$$\lambda = \frac{h \tan \theta}{(h^2 + k^2 + l^2)\, \Delta\theta}$$

where λ is the periodicity in terms of the number of unit cells, θ is the Bragg angle, and h, k, l are Miller indices.

An attempt was made to measure a shift in the value of $\Delta 2\theta$, the difference between the sideband maximum and the $K_{\alpha 1}$ of the Al (200) reflection, during short-time ageing at room temperature in the diffractometer. The experimental scatter was equal to or greater than any changes observed. The scatter results from the low intensity of the sideband as compared to the (200) Al peak intensity.

It was possible, however, to obtain values of $\Delta 2\theta$ as a function of composition, solution-treatment temperature, ageing temperature, and ageing time (at long times). The same experimental problems existed, but the change was well within the measurable range. The periodicities, calculated from Daniel and Lipson's [3] treatment, are listed in table I.

The periodicity of 30% Zn and 38.5% Zn samples aged at 100° C was greater than that of samples aged at 22° C. There was no difference between the 30% Zn alloys treated at the two solution-treatment temperatures. A difference was noted in 38.5% Zn samples aged at a given temperature but solution-treated at different temperatures. The variations were inconsistent in the sense that the wavelength of samples aged at 22° C was greater in samples solution-treated at 435° C, but at 100° C the wavelength was greater in samples solution-treated at 365° C. No difference was found in 50% Zn samples solution-treated at 435° C and aged at 22 and 100° C.

The wavelength increased with ageing time at 100° C but showed no change in either Al/30% Zn or Al/38.5% Zn aged at 22° C for times up to

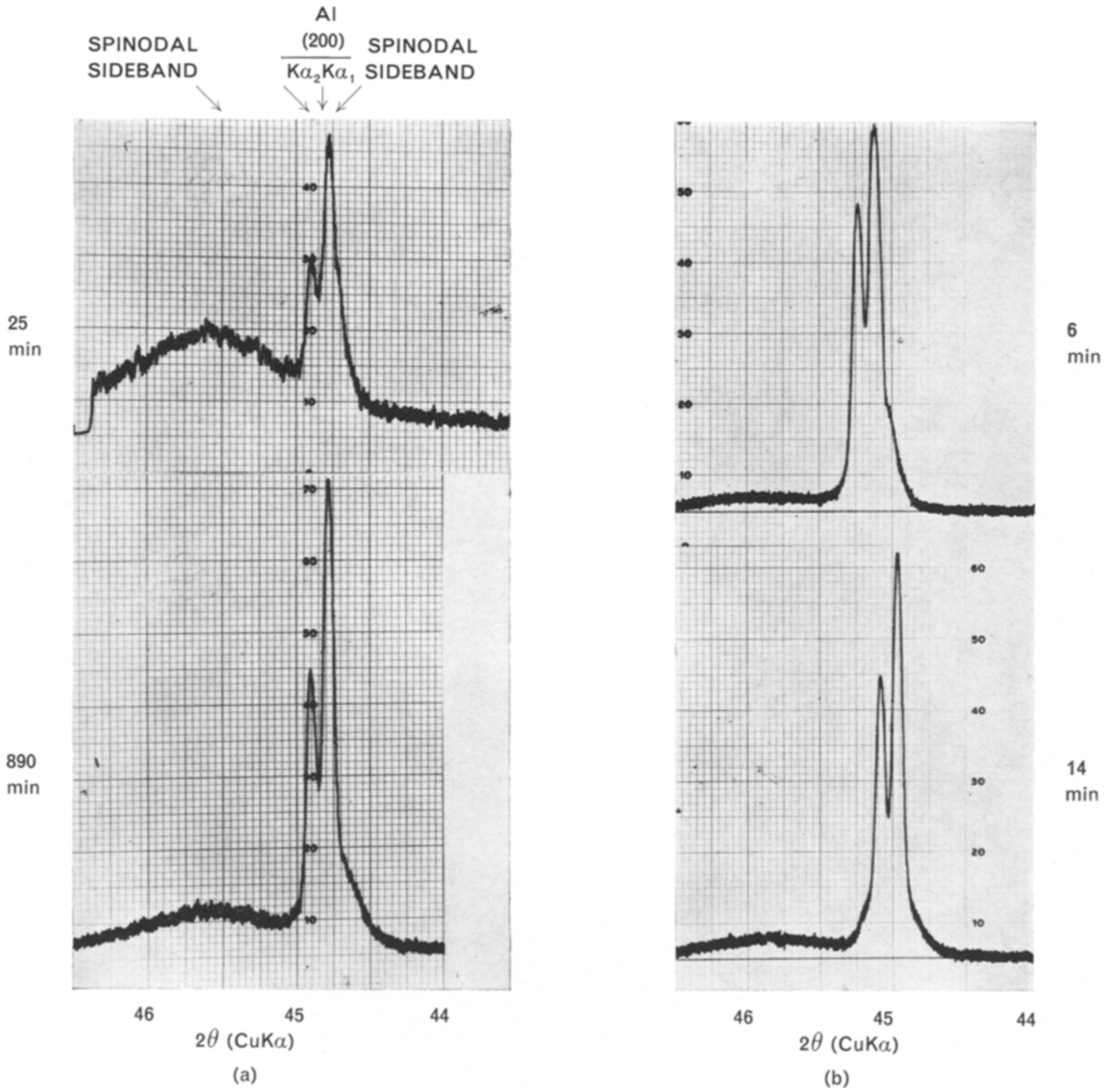


Figure 8 Spinodal sidebands formed on the (200) $_{Al}$ peak in quenched Al/50% Zn during ageing at (a) 22° C and (b) 100° C.

TABLE I Effect of solution-treatment temperature, ageing temperature, and time on spinodal wavelengths in Al/Zn alloys.

Alloy wt % Zn	Solution-treated at 365° C				Solution-treated at 435° C			
	Aged at 22° C		Aged at 100° C		Aged at 22° C		Aged at 100° C	
	Time (min)	λ (Å)	Time (min)	λ (Å)	Time (min)	λ (Å)	Time (min)	λ (Å)
30	100	100 ± 8	100	150	100	100	100	150
30	220 000	100	2600	> 300	220 000	100	1380	235
30	—	—	—	—	—	—	4300	> 300
38.5	100	88	100	190	100	108	10	136
38.5	400 000	100	—	—	400 000	108	230	185
50	—	—	—	—	100	124	10	120
Hybrid-2	—	—	100	210	—	—	—	—

40 weeks. Increasing wavelength is manifested by a decrease in $\Delta 2\theta$; the two peaks come together, and it is nearly impossible to resolve them using copper radiation when $\Delta 2\theta$ is less than about 0.3° 2θ for the (200) Al peak.

4. Discussion

4.1. Ageing Behaviour

The later stages of decomposition of spinodal structures have been discussed theoretically by Cahn [4], who shows that the wavelength increases and that eventually the structure breaks down into the two equilibrium phases. It was found in Al/Zn alloys that the wavelength does increase during ageing at 100° C, and precipitates were observed by electron microscopy in Al/38.5% Zn after 200 min ageing at 100° C [5]. However, sidebands still existed in the alloy when the precipitates were observed, indicating that the wavelength is not very large when the structure breaks up. It is clear, however, that precipitation had started before the modulated structure of the spinodal decomposition was destroyed. The present data were not extensive enough to make a kinetic analysis of wavelength variations.

It has been found in Au/Pt [3] and in Cu/Ni/Fe [7] that ln λ increased with ln t (ageing time) after an initial incubation period. Maximum values of λ of the order of hundreds of Ångströms were reached. Precipitation of the equilibrium phases occurred at the maximum values of λ. Activation energies for the growth of λ were equal to those for interdiffusion in both studies. If we take the values of the interdiffusion coefficient for 18 at. % Zn alloys [8] (close to 38 wt %) and extrapolate to 100° C, a value of 3.5×10^{-17} cm²/sec is obtained. The time required for diffusion over a distance of 100 Å is of the order of 10^4 sec. Examination of thin foils indicated that precipitation had started within 200 min [5] which agrees well with the diffusion time of about 160 min. This calculation is an order of magnitude one only and does not consider the effect of quenched-in vacancies or the annealing out of vacancy loops.

4.2. Anisotropy Effects

Spinodal structures in this study were characterised by an extreme X-ray anisotropy, as shown in fig. 6. This behaviour was always found for all aluminium reflections in all alloys regardless of solution temperature or ageing temperature. The anisotropy disappeared as the spinodal structure broke down by zinc precipitation. The X-ray intensity of the aluminium peaks was markedly reduced during the breakdown, but strangely, the lines that had been well-resolved into the $K_{\alpha 1} - K_{\alpha 2}$ doublet in hardened samples became broad in softened samples and were not resolved in the forward reflection region.

The Laue patterns of samples in the spinodal condition and in the overaged condition were decidedly different [8]. These samples were polycrystalline with an average grain size of about 30 μm. The collimator diameter of the Laue camera was 500 μm, but the divergent spot size was between 1000 and 1500 μm; thus one would expect continuous rings. The Laue pattern of the spinodal structure is that of a pseudo-single crystal or of a very coarse-grain aggregate. On the other hand, the overaged sample shows continuous rings of zinc and nearly continuous rings of aluminium, but there was no change in the grain size of the sample after ageing at 100° C.

In view of the "single crystal" X-ray behaviour it was thought that there might be a mechanical anisotropy. Some existed, but it was not nearly as pronounced as the X-ray effects [1]. Texture studies of the sheet were not made, but it is reasonable to expect some texture in the cold-rolled, recrystallised, and quenched samples that could account for the mechanical anisotropy. However, the X-ray behaviour cannot be accounted for on this basis because the orientation of the grains should not change during overageing at 100° C.

Acknowledgements

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